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Structural and luminescence behavior of the Er^{3+} doped alkali fluoroborate glasses

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ABSTRACT

Er^{3+} doped alkali fluoroborate glasses $B_2O_3 + xCO_3 + NaF + Er_2O_3$ (where x = Li_2, Na_2, K_2, Ca and Mg) have been prepared by following a conventional melt quenching technique. The prepared glasses were investigated through X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), optical absorption and luminescence measurements made at room temperature. The fundamental stretching vibrations of BO_3 and BO_4 structural units in the borate network have been explored through the FTIR spectra. Absorption spectra of the glasses recorded in the ultraviolet–visible region suggest the ionic/covalent nature of the prepared glasses. Oscillator strengths were obtained for the observed absorption transitions. Judd–Ofelt (JO) theory was used to calculate the intensity parameters Ω_λ to analyze the bonding of the Er^{3+} ions with its surrounding ligands. The JO parameters have been used to determine the various radiative parameters like transition probabilities (A), stimulated emission cross-section (σ_P^E), radiative lifetimes (τ_{rad}) and branching ratios (β_R) for the $^2H_{9/2} \rightarrow {}^4I_{15/2}$ and $^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ excited levels of the Er^{3+} ions in the alkali fluoroborate glasses and these results were compared with literature on Er^{3+}:glasses reported earlier. Davis and Mott theory has been used to determine the optical band gap energy (E_{opt}) corresponding to the direct and indirect transitions along with the Urbach energy (ΔE) values for the title glasses. The spectroscopic properties of the prepared glasses have been studied by varying the alkali/alkaline earth elements and the results were discussed and compared with those reported in the literature.

1. Introduction

Over the past several decades rare earth (RE) doped solid state materials have been studied extensively due to their potential applications in the field of lasers, broad band amplifiers, fluorescent labeling and for the design of number of opto-electronic devices [1–6]. Among the glass hosts, silicates (SiO_2), borates (B_2O_3), phosphates (P_2O_5) and tellurites (TeO_2) were identified as conventional glass forming systems due to their good glass forming ability. Of these, borate glasses are the most suitable for the rare earth doping due to their hardness, transparency, resistance towards moisture and chemical durability. However, interest in borate glass is limited due to its high phonon energy. It is difficult to obtain highly efficient infrared and up conversion visible emission of Dy^{3+}, Tb^{3+}, Sm^{3+} and Eu^{3+} ions under normal 4f transitions in the borate glasses and sometimes the relaxation processes that are necessary and beneficial for visible emissions are accelerated. Among lanthanide ions, Er^{3+} has been an important and interesting candidate for use in the broad third communication window [7]. Furthermore the trivalent erbium ion exhibits three fluorescence transitions in blue, green and red in the visible region. The intensity of these transitions could be enhanced by increasing the probability of a particular transition which is the function of ligand field of the surrounding rare earth ions. While designing new laser glasses with higher performance it is essential to understand the relationship between host composition and radiative/non-radiative characters of the Er^{3+} ions. In recent times many researchers have paid much attention to Er-doped tellurite [8,9], bismuthate [10,11], antimony–silicate [12,13] and borate [14–17] based glasses. Although a number of spectroscopic studies on Er doped glasses have been reported, a detailed investigation on structural and optical behaviors of Er^{3+} doped alkali fluoroborate glasses by varying the alkali/alkaline element is yet to understand thoroughly.

The main objective of this work is to (i) prepare Er^{3+}:BxNEr (where x = Li_2, Na_2, K_2, Mg and La) glasses using B_2O_3 as a glass former by following the melt quenching technique, (ii) confirm and analyze the structure of the glasses through XRD and FTIR spectra, (iii) determine the ionic or covalent nature of the prepared glasses and to determine JO intensity parameters through UV–VIS spectra, (iv) determine the radiative properties of the excited states through luminescence spectra, (v) calculate the optical band gap energy (E_{opt}) and Urbach energy (ΔE), and (vi) finally to compare and discuss the results of the Er^{3+} doped alkali fluoroborate glasses with similar studies.

2. Experimental

The Er^{3+} ions doped alkali fluoroborate glasses were prepared by mixing the high purity analytical grade reagents H_3BO_3, Li_2CO_3, Na_2CO_3, K_2CO_3, $MgCO_3$, $CaCO_3$, NaF and Er_2O_3 (all from Aldrich 99.99% pure). The chemical composition studied and their codes are given below.

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$49B_2O_3 + 25Li_2O + 25NaF + 1Er_2O_3$ – – – – – – – – – – – – – – – BLNEr

$49B_2O_3 + 25Na_2O + 25NaF + 1Er_2O_3$ – – – – – – – – – – – – – – – BNNEr

$49B_2O_3 + 25K_2O + 25NaF + 1Er_2O_3$ – – – – – – – – – – – – – – – BKNEr

$49B_2O_3 + 25MgO + 25NaF + 1Er_2O_3$ – – – – – – – – – – – – – – – BMNEr

$49B_2O_3 + 25CaO + 25NaF + 1Er_2O_3$ – – – – – – – – – – – – – – – BCNEr

The above chemical compositions of about 15 g batches were taken in an agate mortar, homogeneously ground and melted in a furnace at a temperature of 950 °C for 45 min. The melt was poured on to a preheated brass plate kept in another furnace maintained at a temperature of 350 °C. These glasses were sufficiently annealed for 8 h and cooled gradually to release the thermal stress associated with the glasses during the quenching process. The glasses were well polished on both sides before measuring their optical properties.

The X-ray diffraction pattern of the prepared glasses has been recorded using JEOL 8530 X-ray diffractometer employing CuK_α radiation. To identify the local structures of the Er^{3+} doped alkali fluoroborate glasses, the FTIR spectra have been recorded with a spectral resolution of 4 cm^{-1} using Perkin-Elmer paragon-500 FTIR spectrophotometer in the wave number range 400–4000 cm^{-1} following KBr pellet technique. Optical absorption measurements were made with a resolution of ±0.1 nm using CARY 500, UV–VIS spectrophotometer in the wavelength range 350–1100 nm. Luminescence spectra of the prepared glasses have been recorded with a spectral resolution of ±1.0 nm using Perkin Elmer LS 55 spectrophotometer in the wavelength range 400–600 nm. All these measurements were carried out at room temperature (RT) only.

The refractive indices (n) of the glass samples were measured using an Abbe refractometer at sodium wavelength (589.3 nm) using monobromonaphthaline as contact liquid. The density of the prepared glasses was determined by following Archimedes method using xylene as an immersion liquid. The other physical properties like polaron radius, interionic distance, field strength, dielectric constant and reflection losses have been calculated based on the formula given in the reported literature [6]. The calculated physical properties of the Er^{3+} doped alkali fluoroborate glasses were presented in Table 1.

3. Results

3.1. Structural analysis

To confirm the amorphous nature of the prepared glasses, X-ray diffraction measurements were carried out and as a representative case, the XRD pattern of the Er^{3+}:BLNEr alkali fluoroborate glass is shown in Fig. 1. The XRD profile of the prepared glasses exhibits a diffused scattering at lower angles ($5° \le \theta \le 80°$) and no diffraction peaks were observed which confirms the amorphous nature of the prepared glasses

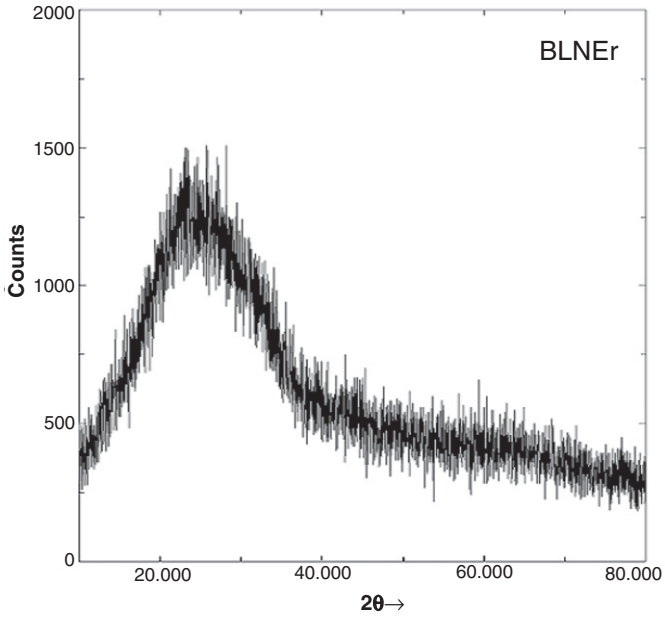

Fig. 1. X-ray diffraction pattern of the Er^{3+} doped alkali fluoroborate glass.

under investigation. The FTIR spectra of prepared Er^{3+}:BxNEr glasses recorded at room temperature are shown in Fig. 2 and their peak assignments are summarized in Table 2. It is observed from Fig. 2 that the addition of alkali/alkaline oxides leads to the formation of several vibrational bands at around 3432, 2927, 2848, 1744, 1633, 1410, 1081, 1018 and 714 cm^{-1}. Further, it can be clearly noticed that all the prepared glasses exhibit absorption bands around 710, 1100 and 1400 $cm^{-}1$ and are mainly attributed due to the presence of B – O – B bending vibrations, B – O stretching vibrations of BO_3 units and B – O stretching vibrations of BO_4 units, respectively [18–23].

3.2. Oscillator strengths and JO parameters

The absorption spectra of the Er^{3+} doped BxNEr alkali fluoroborate glasses recorded in the wavelength range 350–1100 nm are similar to the reported Er^{3+}:glasses [24–26] and the same is shown in Fig. 3. Eleven absorption bands originating from the $^4I_{15/2}$ ground state were identified from the absorption spectra and the same is shown in Fig. 3. The observed transitions are found to be $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $(^2G,^4F)_{9/2}$, $^4G_{11/2}$ and $^2G_{9/2}$ positioned at 10,256, 12,516, 15,361, 18,382, 19,194, 20,492, 22,173, 22,573, 24,570, 26,455 and 27,397 cm^{-1} respectively. Due to the strong absorption in the host matrix, the transitions that are lying above $^2G_{9/2}$ band could not be observed. The band positions along with the assignments for all the title glasses are presented in Table 3 and it is observed from the table that, the band positions of the prepared

Table 1
Physical properties of Er^{3+} doped alkali fluoroborate glasses.

Sl. no.	Physical properties	BLNEr	BNNEr	BMNEr	BKNEr	BCNEr
1	Density ρ(g/cm^3)	3.067 ± 0.098	3.175 ± 0.097	3.309 ± 0.098	3.138 ± 0.088	3.343 ± 0.090
2	Refractive index n_d (589.3 nm)	1.488 ± 0.001	1.481 ± 0.001	1.472 ± 0.001	1.476 ± 0.001	1.469 ± 0.001
3	Er^{3+} ion concentration N × 10^{22} ions/cm^3	0.0585 ± 0.0032	0.0537 ± 0.0030	0.0606 ± 0.0033	0.0477 ± 0.0026	0.0578 ± 0.0030
4	Polaron radius r_p (A°)	4.8161	4.9547	4.7593	5.1552	4.8361
5	Interionic distance ri(A°)	11.952	12.296	11.812	12.794	12.002
6	Field strength F (10^{16} cm^{-2})	0.0209	0.0198	0.0215	0.0183	0.0208
7	Molar refractivity R_m (cm^3)	7.11 ± 0.23	7.08 ± 0.22	6.39 ± 0.19	7.12 ± 0.20	6.55 ± 0.18
8	Dielectric constant (ε)	2.2141	2.1933	2.1667	2.1785	2.1579
9	Reflection losses R (%)	3.8471	3.7586	3.6457	3.6958	3.6083